

Comparison of Small- and Large-scale Ultrafiltration Systems for Organic Carbon and Metals in Freshwater at Low Concentration Factor

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Abstract Interdisciplinary studies on aquatic environments and cross-validation of laboratory vs. field results will likely increase the need for simultaneous use of large- and small-scale ultrafiltration systems. In this study, a comparison of two ultrafiltration systems differing in scale (PrepScale and PelliconXL, Millipore; membrane areas 0.54 m² and 0.005 m², respectively), was made for the cut-offs 3 and 300 kDa. Large systems are useful for their high permeate throughput, while small systems are necessary when the amount of sample is limited. The ability of PrepScale and PelliconXL systems to provide comparable results for organic carbon fractionation was studied for polysaccharide solutions and natural freshwaters. In the latter, the colloidal proportions of different trace metals (V, Cr, Mn, Co, Ni, Cu, Sb, and U) were also determined. Although the colloidal proportions obtained with PelliconXL 3 kDa were sometimes slightly higher than with PrepScale 3 kDa (principally for DOC and U in natural waters), Mann–Whitney statistical test showed

no significant difference in the overall fractionation properties of the two systems. Our observations show that reaching high concentration factors lead to a strong modification of colloids size distribution in the range 50–2,000 nm and thus low concentration factors are preferable to preserve the colloid integrity.

Keywords Colloid separation · Freshwater · Organic carbon · Tangential flow filtration · Trace metals

1 Introduction

Fractionation of water samples by tangential flow filtration (TFF) may require the use of systems differing in membrane surface depending on the analyte of interest and sample availability. According to further use of separated fractions, the required volume may vary from 10 ml to several hundred liters. It is therefore important to ascertain whether large- and small-scale TFF devices provide similar fractionation.

The issue is far from trivial since, despite significant improvements in cleaning and operational procedures, similar fractionation using different systems is not easily achieved (Buessler et al. 1996). Recently, Larsson et al. (2002) defined optimal operational conditions to achieve a correct membrane performance for systems differing in scale, but did not

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directly compare the retention properties and recoveries of small- and large-scale systems.

It is important to note that precise determination of the colloidal proportion of a substance requires the use of the permeation model with time series measurements of the permeate concentrations (e.g. Kilduff and Weber 1992; Guo et al 2000; Wilding et al. 2005). However, we plan to use ultrafiltration as a preparative tool for ecotoxicological tests to evaluate the toxicity of pollutants associated to colloids. Special care should thus be given to preserve the colloid integrity, otherwise the bioavailability of pollutants could be affected, as physical processes inherent to TFF processing (mechanical agitation, heat, or high concentration of colloids) are known to accelerate the coagulation of colloids (Buffle et al. 1992).

The first series of experiments presented here follows the modifications in the colloid size distribution due to ultrafiltration using single particle counter (SPC) and transmission electron microscopy (TEM). The core of the study, then, is a comparison of the retention properties and recoveries of two TFF systems differing in scale for polysaccharide solutions and organic carbon and trace metals in freshwaters.

2 Material and Methods

2.1 Ultrafiltration Procedure

Four Millipore TFF cartridges, were used: two PrepScale (PpS) and two PelliconXL (PXL) with

cut-offs of 3 and 300 kDa. The characteristics and operational parameters of each membrane are summarized in Table 1.

The PpS systems were operated with a peristaltic pump (Watson Marlow 701S) and cleaned following the procedure described by Guéguen et al. (2002). After cleaning, a blank with deionized water was performed and the systems were then preconditioned with 9–10 l of pre-filtered (1.2 µm) sample. Another pre-filtered sample aliquot of 9–10 l was then used for fractionation and analysis. Samples of the feed, retentate and permeate were analyzed for dissolved organic carbon (DOC) and/or trace elements. Feed refers to the initial pre-filtered sample, permeate to the solution that passes through the TFF membrane, and retentate to the solution that does not cross the TFF membrane and where colloids concentrate.

The PXL systems were operated with a peristaltic pump, type Ismatec BVP Standard. The cleaning procedure was very similar to the one used for PpS and consisted of five steps: rinsing the membrane from the storage solution (0.05 M NaOH) with MilliQ water until neutral pH in the permeate; cleaning with 0.5 M HCl (15–20 min); rinsing as above; cleaning with 0.1 M NaOH (15–20 min); and a final rinsing step with MilliQ water. After cleaning, a blank measurement was made with MilliQ water and half to one liter of sample was used to precondition the systems in concentration mode and was then discarded. Another 0.5–1 l was used for fractionation and analysis.

Table 1 Characteristics of membranes and ultrafiltration operational conditions for the different samples (polysaccharide solutions and natural waters)

System	PrepScale (PpS)		PelliconXL (PXL)	
Membrane area	0.54 m ²		0.005 m ²	
Dead volume	250 ml		2–3 ml	
Cut-off	3 kDa	300 kDa	3 kDa	300 kDa
Membrane material	Regenerated cellulose		Regenerated cellulose	
Matrix for polysaccharide solutions	Deionized water		Ultrapure water	
Polysaccharide solutions	Raff (0.6 kDa) D15	D100 D2000	Raff (0.6 kDa) D15	D100 D2000
Natural waters	LG, VR	LG, AR	LG, VR	LG, AR
CF range	2.2–3.2	2.5–3.1	2.0–3.3	2.6–4.6
CFR range	14–21	~ 8	18–33	1–2

Raff=raffinose, D15=dextran 15 kDa, D100=dextran 100 kDa, D2000=dextran 2,000 kDa. LG=Lake Geneva, AR=Arve River and VR=Versoix River. CF=concentration factor, CFR=cross-flow ratio.

2.2 Ultrafiltration Performance

The concentration factors (CF) for colloids were calculated as the ratio between the volumes of feed and retentate. The cross-flow ratios (CFR), calculated as the ratio between the fluxes of retentate and permeate (Larsson et al. 2002), were adjusted to values ≥ 13.9 for the 3 kDa systems by applying flux restrictions on the retentate tubing (Table 1). As already noticed by Larsson et al. (2002), TFF membranes with cut-offs ≥ 100 kDa have high transmembrane fluxes and CFR ≥ 15 cannot be reached. CFR values for the 300 kDa cartridges were calculated only on one occasion (Table 1).

The colloidal concentrations (C_{coll}) of organic carbon and selected metals were calculated as:

$$C_{\text{coll}} = \frac{C_{\text{ret}} - C_{\text{perm}}}{\text{CF}} \quad (1)$$

where C_{ret} and C_{perm} are the analyte concentrations in the integrated samples of retentate and permeate at the end of the fractionation.

Organic carbon and metal recovery (%Recov) and the colloidal proportion of each analyte (%Coll) were calculated as:

$$\% \text{Recov} = 100 \times \frac{C_{\text{coll}} + C_{\text{perm}}}{C_{\text{feed}}} \quad (2)$$

with C_{feed} the concentration of the species in the feed, and

$$\% \text{Coll} = 100 \times \frac{C_{\text{coll}}}{C_{\text{feed}}} \quad (3)$$

For a recovery of 100%, the colloidal concentration is also equal to $C_{\text{feed}} - C_{\text{perm}}$. In such cases, the colloidal proportion (Eq. 3) is equivalent to the retention coefficient RC (e.g., Kilduff and Weber 1992):

$$\text{RC} = 100 \times \left(1 - \frac{C_{\text{perm}}}{C_{\text{feed}}} \right) \quad (4)$$

The colloidal proportion (Eq. 3) depends on feed, retentate and permeate concentrations and on CF through Eq. 1; contrary to RC that depends on C_{perm} and C_{feed} only. We decided to express the species rejection by each membrane with the colloidal proportion since it takes into account all measured critical parameters. When recoveries are around 100%, the two methods give similar results.

2.3 Effects of CF on Colloid Size Distribution

Two independent experiments with water from Versoix River were made at different dates to investigate the effects of CF on the colloid size distribution. They were conducted on 1.2 μm pre-filtered water, and with the 3 kDa PrepScale system for CF = 1.0 (feed), 1.9, 3.1, 4.5 and 10.0 in the first experiment, and CF = 1.0, 2.0, 4.4, and 11.1 in the second. The size distribution was measured in feed, permeate and retentate using the SPC technique which can count individual particles between 50 and 2,000 nm (Rossé and Loizeau 2003). The mass of colloids in each size class was estimated on the assumption that the colloids are spherical and of constant density. Colloid mass recoveries for each size class were then estimated according to formula 2. Total mass recovery was made by comparison of the sum of all size classes at a given CF and at CF = 1 (feed).

At each CF in the first experiment, TEM specimen grids were prepared and observed as described in Chanudet and Filella (2006) to assess changes in colloid structure.

2.4 Polysaccharide Solutions

Solutions of raffinose (Fluka N° 83400) and dextran (Fluka N° 31387–15 kDa; N° 09184–100 kDa; and N° 95771–2,000 kDa) were prepared in about 10 l of deionized water for the PrepScale systems and in 0.5–1 l of ultrapure water (≥ 18 M Ω ; milliQ) for PelliconXL systems (Table 1). No other substance was added to the solutions. Raffinose and dextran concentrations were 5–10 mg/l, corresponding to about 2–4 mg/l of organic carbon, which is in the typical concentration range of natural freshwaters.

2.5 Natural Waters

Waters from the Lake Geneva, the Arve and the Versoix Rivers (Geneva, Switzerland) were collected into two precleaned, Teflon coated bottles of 10 l and pre-filtered within 30 min (CUNO cartridge, Polypro, nominal cut-off 1.2 μm , filter surface ~ 1 m²). Lake Geneva water was sampled in September 2004, at an interval of 1 week for the 3 and 300 kDa systems. It has a typical pH of 8.2, conductivity around 280 $\mu\text{S}/\text{cm}$ and DOC between 0.9 and 1.5 mg/l. The Arve River was sampled in November 2004 and had a pH of 7.8, a

conductivity of 412 $\mu\text{S}/\text{cm}$ and DOC concentration of 1.0 mg/l on the day of sampling. The Versoix River was sampled in August 2006 and had a pH of 8.2, a typical conductivity of 360 $\mu\text{S}/\text{cm}$ approximately and DOC concentration of 2.1–2.4 mg/l.

2.6 Chemical Analyses

For the DOC analysis, sample aliquots of 20–30 ml were acidified to $\text{pH} < 2$ with 2M HCl Suprapur[®], VWR and analyzed immediately or stored at 4°C in the dark pending analysis. The DOC measurements were performed with a Shimadzu High Temperature Total Organic Carbon Analyzer (model 5000). Metals (V, Cr, Mn, Co, Ni, Cu, Sb, and U) were analyzed by ICP-MS (Agilent, HP 4500) on samples acidified at 1% with concentrated HNO_3 (Suprapur[®], VWR). Some other metals were below the detection limits (Al, Ti, Cd, Sn, Pb), suffered strong interferences (Fe) or presented contaminated blanks (Zn) and are not considered. Certified waters for trace metals (SLRS-3 from NRC and 1:10 dilutions of 1643d from NIST) were measured during the analyses and their concentrations were generally within 10% of certified values for concentrations above the quantification value, set as 3.3 times the detection limit. Analytical precision (± 1 s.d.) and mean detection limits for DOC and metals are reported in Appendix 1.

3 Results

3.1 Effect of CF on the Colloidal Size Distribution

In the first experiment (Fig. 1a), one observes (at $\text{CF} = 1.9$ already) a decrease in colloid mass recovery smaller than 400–600 nm and an increase of the larger colloids compared to the feed. When CF rises, the differences to 100% generally get larger. Simultaneously, the total mass of colloids between 50 and 2,000 nm decreases. Thus, only 70% of the original mass of colloids remains at $\text{CF} = 1.9$, 57% at $\text{CF} = 3.1$, 50% at $\text{CF} = 4.5$ and 37% at $\text{CF} = 9.9$. TEM observations (Fig. 2) show the formation of aggregates at $\text{CF} = 1.9$ already and these aggregates tend to increase in number and size with CF. In the second experiment (Fig. 1b), the size distribution at $\text{CF} = 2.0$ is close to that of the feed for sizes $< 1,200$ nm but a decrease in the concentrations of larger colloids is observed. At

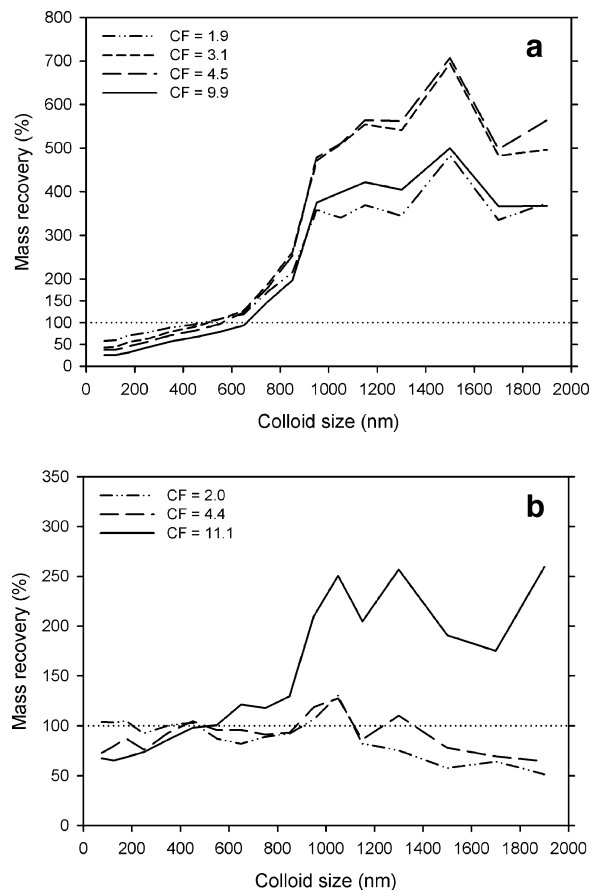


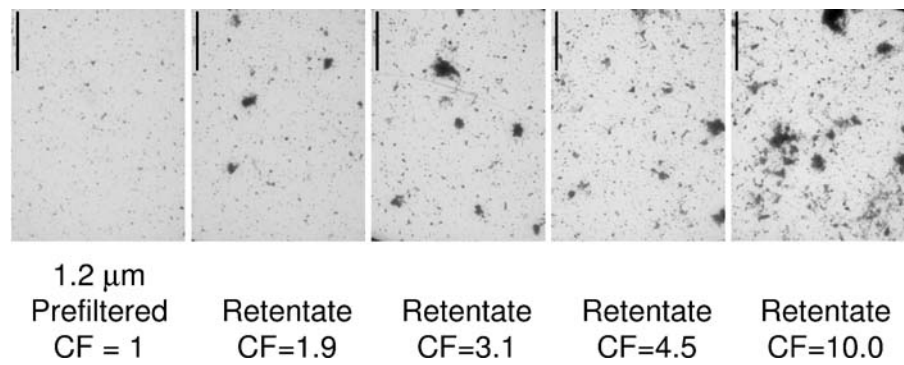
Fig. 1 Colloid mass recoveries (50–2,000 nm) at different CF expressed as percentage of colloid concentration in feed (= 100%, dotted line) at two different dates. Error bars were omitted for clarity; variation coefficients are all $< 10\%$ for 50–900 nm classes, and 10–40% for 900–2,000 classes. CF= concentration factor

this point, the total mass recovery is 99%. At $\text{CF} = 4.4$, concentrations < 300 nm and $> 1,500$ nm show a deficit and the total mass recovery is 80%. At $\text{CF} = 11.1$, the situation of the first experiment is recovered but in a lower extent, i.e. concentrations of small colloids are depleted while these of large ones are increased, and the total mass recovery drops to 72%. Note however that the decrease of total colloidal mass with CF may be due to the inability of the SPC to measure colloids < 50 nm or $> 2,000$ nm and does not necessarily indicate losses to the membrane.

3.2 TFF System Comparison: Polysaccharide Solutions

Recoveries for polysaccharides were between 88 and 107% for all experiments. The 3 kDa membranes retained 7–20% of raffinose and 88–91% of dextran 15 kDa

Fig. 2 TEM micrographs of colloids and particles from feed and retentates at the different concentration factors (CF). Scale bar=20 μm



(Fig. 3a). The 300 kDa membranes retained 6–13% of dextran 100 kDa and 48–60% of dextran 2,000 kDa.

3.3 TFF System Comparison: Natural Waters

Recoveries for organic carbon and trace metals were 85–113% for all experiments (Fig. 3a–d; Appendix 1). In Lake Geneva water and for the 3 kDa cut-off, the colloidal organic carbon (COC) proportion was 55% for the PpS and 63% for the PXL. Colloidal trace metals were generally less than 30% of total concentrations and the calculated differences between the systems were $\leq 10\%$ (Fig. 3b,c,d; Appendix 1). For the 300 kDa cut-off,

the COC proportion was $6 \pm 1\%$ on PpS and $12 \pm 2\%$ on PXL; while all the proportion of colloidal trace metals were $\leq 6 \pm 4\%$ (typical SD).

Water from the Versoix River (fractionated at 3 kDa only) exhibited large differences in COC proportions: 36% for PpS vs. 56% for PXL (Fig. 3a). Similar differences were observed for Cu (Fig. 3c), while the other metals had identical colloidal proportions for both systems (differences $< 10\%$).

Fractionation of Arve River water (300 kDa only) gave a COC proportion of 1–4%. Colloidal proportions of trace metals were $< 5\%$ with little differences between the systems.

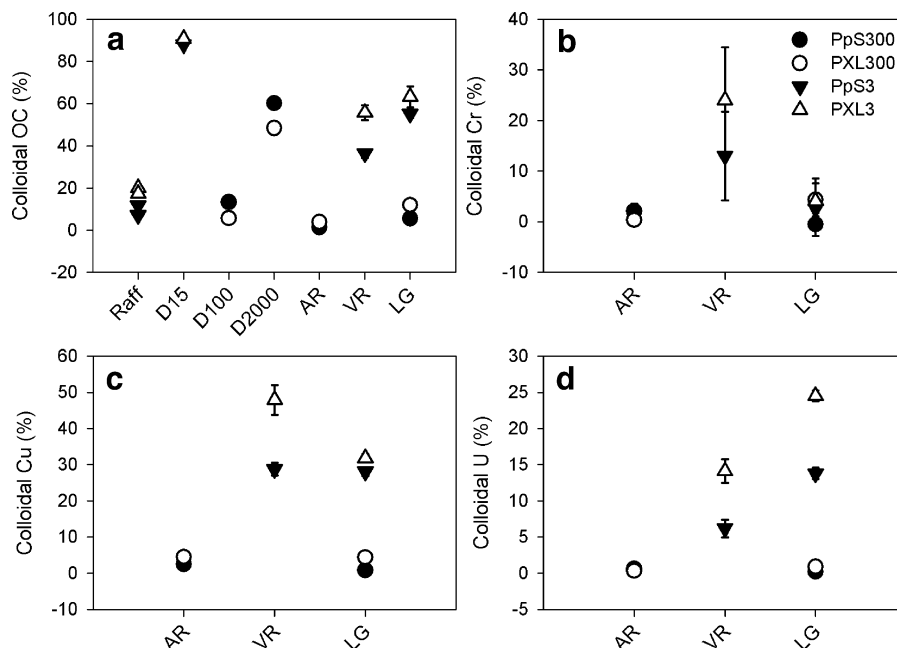


Fig. 3 Summary of the colloidal proportion of organic carbon (a), chromium (b), copper (c), and uranium (d). Error bars represent the propagated analytical standard error. Abbreviations are as follows: PpS=PrepScale (large system), PXL=PelliconXL (small system), 3 and 300 are the membrane nominal cut-offs (in

kDa); Raff=raffinose; D15, D100, and D2000=dextran of 15, 100, and 2,000 kDa, respectively; AR=Arve River; VR=Versoix River; and LG=Lake Geneva. Notes: raffinose was measured twice; AR and VR fractionations were only performed with 300 and 3 kDa, respectively, the panels have different vertical scales

4 Discussion

4.1 Choice of Concentration Factor

SPC and TEM results show that, during TFF, changes in both colloid size distribution and total mass recovery become more important with increasing concentration factors (Figs. 1 and 2). As excessive colloid aggregation in the retentate might change the bioavailability of test substances and thus bias the biotests that will be performed in the future, we decided to work at low CF for the comparison between the large and small TFF systems. We acknowledge that the use of low CF may overestimate the colloidal proportion of organic carbon and metals (e.g. Guo et al. 2000; Wilding et al. 2005). However, the use of low CF should not invalidate the comparison between TFF systems because the CF used for the fractionation of each sample were similar for both large- and small-scale systems (Appendix 1).

4.2 Overall Performance of Membranes

Overall DOC fractionation (polysaccharides and freshwaters) was not statistically different between PpS and PXL systems (Mann–Whitney rank test, $p=1.000$ for 300 kDa, $p=0.421$ for 3 kDa). For freshwaters, the same test applied to DOC and trace metals together showed no difference except for Lake Geneva at 300 kDa ($p=0.038$). For this particular case, however, most colloidal proportions were 0–5%, so that this difference cannot be considered as operationally significant.

4.3 Retention of Polysaccharides

Polysaccharide recoveries (88–107%) were acceptable for both 3 and 300 kDa even though CFR were much lower than 15 for the 300 kDa systems. PpS and PXL systems retained the polysaccharides in a very similar manner (Fig. 3a). The mean difference in COC proportions was 8% for both 3 and 300 kDa systems, the highest difference being for the first raffinose measurement (7% for PpS 3 kDa and 20% for PXL 3 kDa). In the case of raffinose, the impact of slight contamination or loss may be dramatic given that this sugar has very low molecular weight and feed and permeate concentrations are very close.

The colloidal proportion of dextran 2,000 kDa obtained with the 300 kDa systems was surprisingly low (48–60%). The high polydispersity of the dextran 2,000 kDa used in these experiments (weight-average molecular weight=2,537 kDa; number-average molecular weight=242.2 kDa according to the certificate of analysis) or of the membrane pores can explain this result. However, for this study, the relevant point is that the two systems showed similar fractionation properties.

For comparison, Guéguen et al. (2002) found a retention coefficient of raffinose around 15% for a 1 kDa, regenerated cellulose membrane, and Larsson et al (2002), using a 100 kDa membrane, reported a retention of 54 and 98% for 10 and 70 kDa dextrans, respectively.

4.4 Retention of Natural Waters

Recoveries of DOC and metals were acceptable ($100\pm13\%$) even for the low CFR of the 300 kDa cartridges. Differences in colloidal proportions for individual metals and for DOC were generally $\leq 10\%$ except for DOC and Cu in the Versoix River (Fig. 3a,c; Appendix 1), and are possibly due to differences in recoveries between the two systems. DOC recovery was 87% for PpS and 102% for PXL. If the losses observed for PpS were attributed to the colloidal fraction only, then the COC fraction for the PpS would rise from 36% to 50%; very close to the 56% calculated for PXL. A similar reasoning applies for Cu.

V and Sb have colloidal proportions lower than 10%. These results are in agreement with their general occurrence as anionic complexes in circumneutral freshwaters (Stumm and Morgan 1996; Filella et al. 2002) and with literature results (e.g., Pokrovsky et al. 2006). Anionic complexes adsorb poorly on natural colloids which generally have a negative net charge. Uranium, which also forms anionic complexes (principally $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ in carbonated waters; Stumm and Morgan 1996), is retained in larger proportions (Fig. 3d). Possible explanations are membrane rejection due to the rather strong negative charge of uranyl complexes (Guo et al. 2001), the molecular weight of the U carbonate complexes (around 0.4 kDa; i.e. close to that of raffinose), and/or adsorption on iron oxides (Jung et al. 1999). The retention of U on the PXL 3 kDa is 6–10% higher

than on the PpS despite good recoveries (97–100%). This might be attributed to a small difference in the separation properties between the two systems for U carbonate complexes. The case of chromium (Fig. 3b) is more complex as Cr(III) generally forms cationic or neutral species and Cr(VI) anionic ones. Colloidal Cr was found to be negligible in the Lake Geneva even with the 3 kDa systems, but present at 14–24% in the Versoix River for PpS and PXL. The results of Li and Xue (2001) would suggest that the majority of this element exists as Cr(III) in the waters of Lake Geneva. Evidence exists that Cr(III) can occur in both colloidal and truly dissolved fractions (Bobrowski et al. 2004). Manganese is mostly present as truly dissolved, with a maximal colloidal proportion in the 3 kDa–1.2 μm range, of 12% in Lake Geneva, in agreement with previous studies (Jaïry et al. 1999; Pokrovsky et al. 2006). Less than 11% of Ni and Co are present in the 3 kDa–1.2 μm fraction of Arve River and around 20% of Ni was in this fraction for Lake Geneva consistently with the low partition coefficients between truly dissolved and colloidal phases calculated by Pokrovsky et al. (2006).

5 Conclusions and Outlook

For the operational conditions and the samples used in this study, the differences of configuration and hydrodynamics between the two types of membranes

do not seem to significantly influence fractionation properties, so that the large- and small-scale can be used indifferently.

These observations are important since the combined use of small- and large-scale TFF systems is likely to increase in the future for example to compare trace metal bioavailability in the field and in laboratory experiments, or organic carbon and element partitioning in surface and pore waters. In such experiments, the availability of TFF systems with comparable fractionation properties will clearly be a necessary condition for any meaningful interpretation of experimental results.

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Appendix 1

DOC and trace metal concentrations measured in the feed, retentate (Ret) and permeate (Perm) for fractionation of natural waters. Concentrations are the mean of duplicate analysis and the standard deviation values are $1\times$ propagated analytical errors (Err). All concentrations in $\mu\text{g/l}$ except for DOC (mg/l). Recoveries (%Recov) and colloidal proportions (%Coll) are calculated using formulas 2 and 3 in the main text. n.m. stands for “not measured.”

	LOD	Lake Geneva, 3kDa						Versoix River, 3kDa								
		PrepScale, CF = 3.22			PelliconXL, CF = 2.89			PrepScale, CF = 3.13			PelliconXL, CF = 3.32					
		Feed	Ret	Perm	% recov	% coll	Feed	Ret	Perm	% recov	% coll	Feed	Ret	Perm	% recov	% coll
DOC	0.1	1.10	2.51	0.56	106	55.2	1.10	2.53	0.53	112	63.2	2.41	3.96	1.22	87	36.4
Err DOC		0.03	0.05	0.01	3	2.0	0.03	0.15	0.02	6	5.0	0.12	0.06	0.04	5	2.0
V	0.07	0.15	0.15	0.13	89	6.0	0.15	0.16	0.12	88	7.6	0.31	0.34	0.27	93	7.7
Err V		0.01	0.00	0.00	6	1.3	0.01	0.00	0.00	5	1.2	0.01	0.01	0.01	6	1.8
Cr	0.14	0.38	0.45	0.42	111	2.6	0.38	0.46	0.41	112	4.1	0.89	1.11	0.75	97	13.0
Err Cr		0.06	0.02	0.03	20	3.1	0.06	0.04	0.03	20	4.4	0.15	0.04	0.23	32	8.7
Mn	0.27	0.46	0.53	0.35	89	11.8	0.46	0.53	0.37	93	12.2	2.58	2.53	2.04	85	6.0
Err Mn		0.03	0.02	0.02	8	2.3	0.03	0.03	0.01	7	2.7	0.14	0.07	0.04	5	1.1
Co	0.01	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0.10	0.13	0.09	97	11.1
Err Co		n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0.01	0.01	0.00	10	2.9
Ni	0.17	0.81	1.11	0.63	96	18.3	0.81	1.22	0.69	108	22.8	1.10	1.17	0.89	89	7.9
Err Ni		0.02	0.04	0.04	6	2.1	0.02	0.04	0.01	4	1.8	0.07	0.04	0.08	10	2.7
Cu	0.23	0.97	1.62	0.74	104	28.1	0.97	1.53	0.63	97	31.8	0.74	1.12	0.45	90	28.8
Err Cu		0.02	0.02	0.02	3	1.1	0.02	0.02	0.01	3	1.2	0.02	0.04	0.01	3	1.8
Sb	0.012	0.11	0.13	0.13	113	-0.8	0.11	0.13	0.10	94	8.7	0.10	0.09	0.07	71	7.9
Err Sb		0.01	0.01	0.03	25	-7.3	0.01	0.00	0.00	7	1.9	0.02	0.02	0.01	18	6.9
U	0.01	1.82	2.37	1.56	100	13.8	1.82	2.61	1.32	97	24.5	0.33	0.36	0.30	98	6.2
Err U		0.03	0.04	0.02	2	0.8	0.03	0.02	0.02	2	0.8	0.01	0.01	0.01	4	1.2

	LOD	Lake Geneva, 300 kDa						Arve River, 300 kDa								
		PrepScale, CF = 2.88			PelliconXL, CF = 2.63			PrepScale, CF = 3.09			PelliconXL, CF = 3.61					
		Feed	Ret	Perm	% recov	% coll	Feed	Ret	Perm	% recov	% coll	Feed	Ret	Perm	% recov	% coll
DOC	0.1	0.98	1.03	0.87	94	5.6	0.98	1.15	0.84	97	12.0	1.02	1.02	0.98	97	1.4
Err DOC		0.03	0.03	0.01	3	1.2	0.03	0.04	0.02	4	1.9	0.05	0.04	0.03	6	1.7
V	0.07	0.14	0.13	0.13	93	0.6	0.14	0.14	0.13	95	2.2	0.14	0.15	0.14	96	2.6
Err V		0.01	0.01	0.00	5	1.6	0.01	0.00	0.00	5	1.7	0.00	0.00	0.00	4	1.4
Cr	0.14	0.84	0.90	0.92	109	-0.5	0.84	0.94	0.84	105	4.4	0.59	0.61	0.57	99	2.0
Err Cr		0.05	0.02	0.05	10	-2.3	0.05	0.05	0.05	9	3.3	0.02	0.01	0.02	5	1.5
Mn	0.27	0.41	0.38	0.37	91	0.8	0.41	0.41	0.35	92	5.1	7.13	7.17	6.81	97	1.6
Err Mn		0.02	0.02	0.02	6	2.1	0.02	0.02	0.03	9	3.5	0.12	0.11	0.17	3	0.9
Co	0.01	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0.26	0.26	0.25	97	1.7
Err Co		n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	0.01	0.01	0.01	5	1.7
Ni	0.17	1.02	0.93	0.95	93	-0.7	1.02	1.00	0.84	89	5.8	11.2	10.2	9.4	86	2.5
Err Ni		0.06	0.04	0.03	6	-1.7	0.06	0.03	0.03	6	1.6	0.25	0.24	0.22	3	0.9
Cu	0.23	1.17	1.10	1.07	93	0.8	1.17	1.14	1.00	90	4.4	3.15	2.94	2.70	88	2.4
Err Cu		0.03	0.03	0.01	3	1.0	0.03	0.04	0.02	3	1.4	0.03	0.05	0.07	3	0.9
Sb	0.012	0.11	0.11	0.11	104	0.7	0.11	0.11	0.11	100	-0.6	0.18	0.18	0.17	99	0.9
Err Sb		0.01	0.01	0.01	10	3.8	0.01	0.01	0.00	9	-2.9	0.01	0.01	0.01	5	1.6
U	0.01	1.85	1.81	1.80	98	0.2	1.85	1.86	1.81	99	0.9	2.30	2.28	2.24	98	0.6
Err U		0.03	0.03	0.02	2	0.6	0.03	0.04	0.01	2	0.8	0.02	0.02	0.01	1	0.4

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